

CD221. LECTURE 16. CLASSICAL STATISTICAL MECHANICS

• Classical Statistical Mechanics

As we've seen, statistical mechanics is all about counting states and adding them up in some way. Up to now, these states have typically been *discrete* quantum mechanical states. For the ideal gas, for example, they were the quantized energy states of the particle in a box. For the Einstein solid, they were the quantized energy states of a harmonic oscillator. But since we're dealing with macroscopic objects, with large numbers of particles, and at temperatures that are typically quite high, it seems as though it shouldn't be necessary to start with a quantum mechanical description of the system at all. So it's natural to ask if there's a way to recast our existing statistical mechanical formalism in language more suited to the description of particles at a classical level.

Recall that a microstate is a specification of some property of the individual constituents of a macroscopic system. In classical mechanics, it is the set of positions \mathbf{q}_i and momenta \mathbf{p}_i of all $i=1$ to N particles at some instant of time that constitutes a complete microscopic description of the system. That is,

$$\text{Classical microstate} \leftrightarrow q_{1x}, q_{1y}, q_{1z}, p_{1x}, p_{1y}, p_{1z}, \dots, q_{Nx}, q_{Ny}, q_{Nz}, p_{Nx}, p_{Ny}, p_{Nz} \quad (2)$$

It is often useful to think of this set of $3N$ positions and $3N$ momenta as a single point in an abstract space – called the phase space – that is defined by a set of $6N$ mutually perpendicular axes, one each for the 3 components of all particle positions and one each for the 3 components of all momenta. This single point – a phase point – represents a unique microstate at some instant of time. Because the \mathbf{q}_i and \mathbf{p}_i evolve in time under the action of the classical equations of motion, the phase point moves too, tracing out a complicated trajectory through phase space.

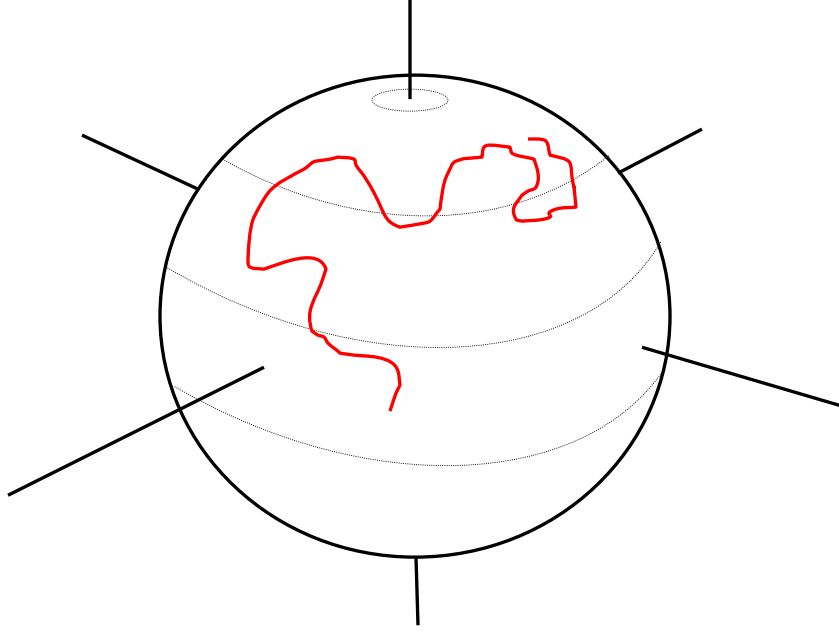
1. The Classical Microcanonical Partition Function

Now consider a system of constant energy U at some fixed V and N . U is clearly a function of \mathbf{q}_i and \mathbf{p}_i . That is,

$$U = U(\{\mathbf{q}_i\}, \{\mathbf{p}_i\}) \quad (3)$$

where the braces denote “the set of”. The phase space trajectory of such a system takes place on a hypersurface of $6N-1$ dimensions (because the existence of a relation between the \mathbf{q}_i and \mathbf{p}_i , as defined by Eq. (3), reduces by one the total number of degrees of freedom, just as a particle in 2 dimensions satisfying $x^2 + y^2 = r^2$ has only 1 degree

of freedom, not 2, and is constrained to lie on a circle.) The nature of this hypersurface and a typical phase trajectory on it are depicted schematically below:



The classical analogue of the assumption of equal à priori probabilities is that the phase space trajectory above can pass through any of the points on the hypersurface with equal probability. So the “area” of this surface is a measure of the number of classical microstates there are. So we expect that we can determine this number, Ω (in general a function of U , V and N) by integrating (i.e., adding up) the \mathbf{q}_i and \mathbf{p}_i over those values that satisfy Eq. (3). In other words,

$$\Omega = \frac{1}{N!} \int dq_{1x} \int dq_{1y} \int dq_{1z} \int dp_{1x} \int dp_{1y} \int dp_{1z} \cdots \int dq_{Nx} \int dq_{Ny} \int dq_{Nz} \int dp_{Nx} \int dp_{Ny} \int^* dp_{Nz} \quad (4)$$

where the asterisk on the last integral signifies that the integrations are to be carried out subject to the restriction mentioned above, and where the factorial term is introduced to account for the indistinguishability of the particles.

However, Eq. (4) cannot be the whole story since the right hand side has dimensions (i.e., units) while the left hand side does not. Eq. (4) must therefore include some factor that makes it dimensionless. As it happens, the units of the product of position and momentum are exactly the same as the units of Planck’s constant h , and since we know that Planck’s constant should appear in our final expressions, we tentatively amend Eq. (4) to

$$\Omega = \frac{1}{N!h^{3N}} \int d^3 q_1 \int d^3 p_1 \cdots \int d^3 q_N \int^* d^3 p_N \quad (5)$$

where, in order to keep the expression compact, we've introduced the notation $d^3 p_i$ for $dp_{ix} dp_{iy} dp_{iz}$ and $d^3 q_i$ for $dq_{ix} dq_{iy} dq_{iz}$, for all $i=1,2,\dots,N$. If Eq. (5) is now the correct classical description of Ω , we should be able to apply it to some system for which we already know Ω from a *quantum mechanical* counting of microstates and get the same answer. The obvious choice of system is the ideal gas.

But before we get to this system, let's first recall that in general the classical energy of a collection of N particles is just the sum of the kinetic and potential energies of each. This sum, called the *Hamiltonian*, and denoted H (not to be confused with enthalpy!) takes the form

$$H = \frac{1}{2m} \sum_{i=1}^N \sum_{\alpha=x,y,z} p_{i\alpha}^2 + V(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N) \quad (6)$$

where the first term on the right hand side corresponds to the particles' kinetic energy and the second term to their potential energy. For an ideal gas V is 0. (The choice of V to denote potential energy is a little unfortunate since we've been using it all this while to stand for volume, but hopefully the context will make the distinction clear.)

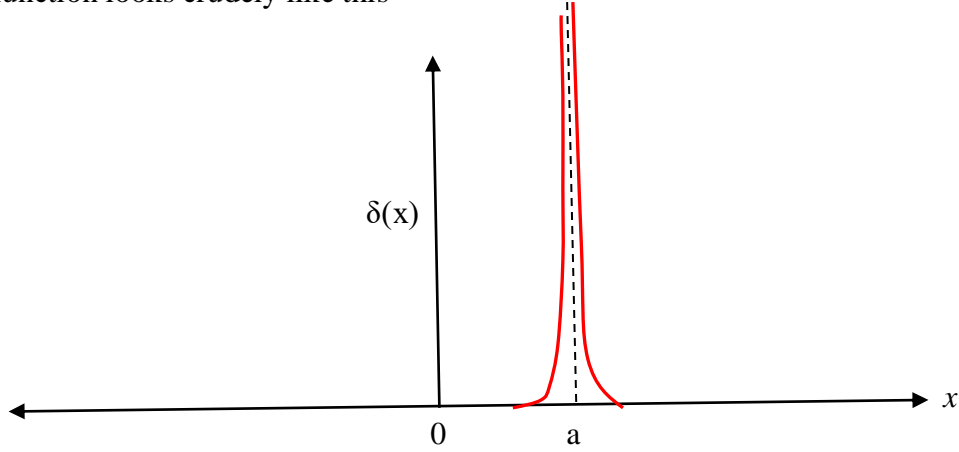
So if a macroscopic system of N interacting particles is found to have the energy U , then its Hamiltonian H [Eq. (6)] must equal U . We can calculate how many of the system's microstates have an energy U using Eq. (5) but the calculation requires the evaluation of the $6N$ integrals in such a way that the equality $H=U$ is satisfied. In general, this is difficult to do, but there's a mathematical trick that simplifies the problem. The trick is to make use of something called the delta function, denoted $\delta(x-a)$, where x is a variable and a is a constant. Loosely speaking, $\delta(x-a)$ is defined by these two properties

$$\delta(x-a) = \delta(a-x) = \begin{cases} \infty, & x = a \\ 0, & x \neq a \end{cases} \quad (7a)$$

and

$$\int_{-\infty}^{\infty} dx \delta(x-a) = 1 \quad (7b)$$

So the function looks crudely like this



It's infinitely tall and infinitely thin, but it has unit area. As a consequence of (7a) and (7b), $\delta(x - a)$ has this additional property:

$$\int_{-\infty}^{\infty} dx f(x) \delta(x - a) = f(a) \quad (7c)$$

where $f(x)$ is any arbitrary function of x , and $f(a)$ is the value of $f(x)$ when x is replaced everywhere by a . In a sense, the delta function is a counting machine – it delivers an output only when $x = a$; when $x \neq a$, the output is 0.

These properties of the delta function make it possible to rewrite the expression for Ω [Eq. (5)] as

$$\Omega = \frac{1}{N! h^{3N}} \int d^3 q_1 \int d^3 p_1 \cdots \int d^3 q_N \int d^3 p_N \delta(U - H(\{\mathbf{q}_i\}, \{\mathbf{p}_i\})) \quad (8)$$

where there is no longer any need to restrict the range of integrations to those values of \mathbf{q}_i and \mathbf{p}_i that satisfy Eq. (3) because the restriction is automatically enforced by the delta function, which delivers an output (i.e., counts a microstate) when $H = U$ but doesn't when $H \neq U$.

With these preliminaries, we can now specialize to the case of the ideal gas. For this system, as noted before, $V = 0$, since the particles are non-interacting. So Eq. (8) becomes

$$\Omega = \frac{1}{N! h^{3N}} \int d^3 q_1 \cdots \int d^3 q_N \int d^3 p_1 \cdots \int d^3 p_N \delta(U - [\mathbf{p}_1^2 + \mathbf{p}_2^2 + \cdots + \mathbf{p}_N^2]/2m) \quad (9)$$

Because the integrand does not depend on the \mathbf{q}_i , the spatial integrals can be carried out immediately. Along each Cartesian axis, a given position coordinate ranges across the length L of one side of the box that holds the gas. Hence, $\int d^3 q_i = L^3 = V$, and the N position coordinates together contribute a factor of V^N . So Eq. (9) now becomes

$$\Omega = \frac{V^N}{N!h^{3N}} \int d^3 p_1 \cdots \int d^3 p_N \delta(U - [\mathbf{p}_1^2 + \mathbf{p}_2^2 + \cdots + \mathbf{p}_N^2]/2m) \quad (10)$$

The momentum integrals present more of a problem, but they're carried out by transforming to a new set of variables. The transformation is defined as follows:

$$(p_{1x}, p_{1y}, p_{1z}, \dots, p_{Nx}, p_{Ny}, p_{Nz}) \rightarrow (p, \phi, \theta_1, \theta_2, \dots, \theta_{3N-3}, \theta_{3N-2}) \quad (11)$$

where p is the magnitude of the vector $\mathbf{p}_1^2 + \mathbf{p}_2^2 + \cdots + \mathbf{p}_N^2$, i.e., $p = \sqrt{\mathbf{p}_1^2 + \mathbf{p}_2^2 + \cdots + \mathbf{p}_N^2}$, and $\phi, \theta_1, \theta_2, \dots, \theta_{3N-3}, \theta_{3N-2}$ are all angles. These new variables are limited to the following intervals:

$$0 \leq p \leq \infty; \quad 0 \leq \phi \leq 2\pi; \quad 0 \leq \theta_i \leq \pi, \quad i = 1, 2, \dots, 3N-2 \quad (12)$$

After making the transformation to these new variables, the integration element itself is changed to

$$dp_{1x} dp_{1y} dp_{1z} \cdots dp_{Nx} dp_{Ny} dp_{Nz} \rightarrow p^{3N-1} dp d\phi \sin \theta_1 d\theta_1 \sin^2 \theta_2 d\theta_2 \cdots (\sin \theta_{3N-2})^{3N-2} d\theta_{3N-2} \quad (13)$$

and so Eq. (10) now becomes

$$\Omega = \frac{V^N}{N!h^{3N}} \int_0^\infty dp p^{3N-1} \int_0^{2\pi} d\phi \int_0^\pi d\theta_1 \sin \theta_1 \int_0^\pi d\theta_2 \sin^2 \theta_1 \cdots \int_0^\pi d\theta_{3N-2} \sin^{3N-2} \theta_{3N-2} \delta(U - p^2/2m) \quad (14)$$

which doesn't look any less complicated than the integral we had before but it actually is because the integrand contains just a single variable (viz., p) instead of $3N$ variables. Furthermore all the angular integrations can be carried out exactly. The ϕ integral is of course trivial – it immediately yields 2π . The θ integrals can be written compactly as

$$I_\theta \equiv \int_0^\pi d\theta_1 \sin \theta_1 \int_0^\pi d\theta_2 \sin^2 \theta_1 \cdots \int_0^\pi d\theta_{3N-2} \sin^{3N-2} \theta_{3N-2} = \prod_{k=1}^{3N-2} \int_0^\pi d\theta_k \sin^k \theta_k \quad (15)$$

and the last integral (on the right) is actually known in closed form; it is given by

$$\int_0^\pi d\theta_k \sin^k \theta_k = \frac{\sqrt{\pi} \Gamma((k+1)/2)}{\Gamma((k+2)/2)} \quad (16)$$

and so

$$\begin{aligned} I_\theta &= \prod_{k=1}^{3N-2} \frac{\sqrt{\pi} \Gamma((k+1)/2)}{\Gamma((k+2)/2)} \\ &= \pi^{(3N-2)/2} \frac{\Gamma(1)\Gamma(3/2)\Gamma(2)\Gamma(5/2)\cdots\Gamma((3N-2)/2)\Gamma((3N-1)/2)}{\Gamma(3/2)\Gamma(2)\Gamma(5/2)\cdots\Gamma((3N-1)/2)\Gamma(3N/2)} \\ &= \frac{\pi^{3N/2-1}}{\Gamma(3N/2)} \end{aligned} \quad (17)$$

After the results of the angular integrations are put back into Eq. (14), Ω is reduced to

$$\Omega = \frac{2\pi^{3N/2} V^N}{N! h^{3N} \Gamma(3N/2)} \int_0^\infty dp p^{3N-1} \delta(U - p^2/2m) \quad (18)$$

A final change of variables, defined by $x = p^2/2m$, transforms Eq. (18) to

$$\Omega = \frac{(2\pi m)^{3N/2} V^N}{N! h^{3N} \Gamma(3N/2)} \int_0^\infty dx x^{3N/2-1} \delta(U - x) \quad (19)$$

The property of the delta function [Eq. (7c)] makes this last integral trivial, and we're finally left with

$$\Omega(U, V, N) = \frac{(2\pi m)^{3N/2} V^N U^{3N/2-1}}{N! h^{3N} \Gamma(3N/2)} \quad (20)$$

If you compare Eq. (20) with Eq. (16) in Lecture 12, where we had calculated the microcanonical partition function of the ideal gas starting from the energy eigenstates of a particle in a box, you'll see that the two are virtually identically, and that for all practical purposes they *are* identical because N is enormous (making $3N/2 \pm 1 = 3N/2$.)

So the correspondence we have suggested between sums over quantum mechanical microstates and integrals over phase space seems to be sound, and we can expect to apply it to the canonical, grand canonical and isothermal-isobaric formalisms as well. In the next section we'll check that this expectation is in fact borne out for the case of the ideal gas treated by the classical canonical formalism.

2. The Classical Canonical Partition Function

Instead of being at constant U (at fixed V and N), suppose the system under consideration is at constant T , again at fixed V and N . In this case, we've seen that the connection between the system's quantum mechanical microstates α and its thermodynamic properties is through the canonical partition function $Q = \sum_{\alpha} e^{-\beta U_{\alpha}}$. Based on our treatment of Ω , we expect that the canonical partition function of a system of N indistinguishable particles described classically by their phase space variables can be defined as

$$Q = \frac{1}{N!h^{3N}} \int d^3 p_1 \int d^3 q_1 \cdots \int d^3 p_N \int d^3 q_N e^{-\beta H} \quad (21)$$

Let's apply this formula to the ideal gas, and see if it gives the expected results. Since an ideal gas has no inter-particle interactions, its potential energy V is 0, and its Hamiltonian therefore is

$$H = \frac{1}{2m} [p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + \cdots + p_{Nx}^2 + p_{Ny}^2 + p_{Nz}^2] \quad (22)$$

Substituting Eq. (22) into Eq. (21), we have

$$Q = \frac{1}{N!h^{3N}} \int d^3 p_1 \cdots \int d^3 p_N e^{-\beta [p_1^2 + \cdots + p_N^2]} \int d^3 q_1 \cdots \int d^3 q_N \quad (23)$$

where we've separated out the position and momentum integrals. The position integrals are of exactly the same form as those we'd evaluated in our calculation of Ω . Hence,

$$\int d^3 q_1 \cdots \int d^3 q_N = (L^3)^N = V^N \quad (24)$$

Coming to the momentum integrals, we see that along each Cartesian coordinate, the momentum integral of a given particle (which is separable from all the rest) is a Gaussian integral. And so for particle 1, say,

$$\int_{-\infty}^{\infty} dp_{1x} e^{-\beta p_{1x}^2 / 2m} = \sqrt{2\pi m k_B T} \quad (25)$$

Identical results are obtained for the momentum integrals of all the other particles. Combining these results with Eq. (24) and substituting into Eq. (23), we find that

$$Q = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} V^N \quad (26)$$

which is indeed identical to the result we'd obtained earlier on the basis of a sum over quantum mechanical microstates.

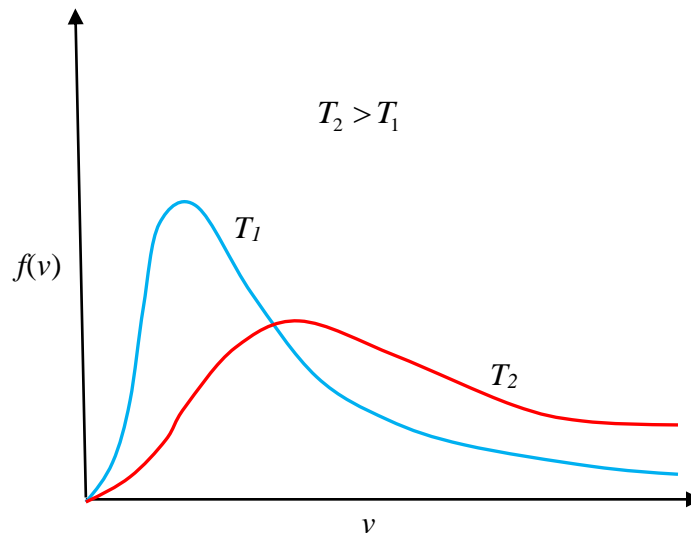
The classical counterparts of the grand canonical and the isothermal-isobaric partition functions can be defined along the same lines, as integrals over phase space of an appropriate Hamiltonian, but we won't consider them here.

- Some Applications of Classical Statistical Mechanics

Now that we've figured out how to formulate statistical mechanics in the language of classical mechanics, there are a number of results dealing with bulk behavior that are fairly easily derived. One of these concerns the distribution of the speeds of gas molecules in a container of fixed volume V at some constant temperature T . This distribution is known as the Maxwell-Boltzmann distribution, and its derivation is described below.

- (i) Maxwell-Boltzmann distribution

In any sample of gas at temperature T , not all molecules will travel with the same speed. The fraction f of molecules with a *given* speed can be determined experimentally, and this fraction, as the function of the speed, and at two different temperatures T_1 and T_2 , with $T_2 > T_1$, looks roughly like this:



The fraction of molecules with a given speed can be interpreted as the probability p that any *one* particle will have that speed, which suggests that it should be possible to calculate p from statistical mechanics. To apply the method, we need to first assign a probability that at constant T , the system occupies a particular phase point. Since we know that for the system to occupy a particular quantum mechanical microstate α , the probability p_α is

$$p_\alpha = \frac{e^{-\beta U_\alpha}}{Q}$$

we expect that the corresponding classical analogue is

$$p(\{\mathbf{q}_i\}, \{\mathbf{p}_i\}) = \frac{1}{N!h^{3N}} \frac{e^{-\beta H(\{\mathbf{q}_i\}, \{\mathbf{p}_i\})}}{Q} \quad (27)$$

which is properly normalized, as it should be. From this expression, to calculate the probability that any one particle, say the k th, has a certain momentum \mathbf{p}_k , one has to integrate over the positions and momenta of all but the k th particle. That is,

$$\begin{aligned} p(\mathbf{p}_k) &= \frac{1}{N!h^{3N}} \frac{\left(\prod_{i \neq k}^N \int_{-\infty}^{\infty} d^3 p_i e^{-\beta \mathbf{p}_i^2 / 2m} \right) e^{-\beta \mathbf{p}_k^2 / 2m} \prod_{i=1}^N \int d^3 q_i}{\frac{1}{N!h^{3N}} (2\pi m k_B T)^{3N/2} V^N} \\ &= \frac{e^{-\beta \mathbf{p}_k^2 / 2m}}{(2\pi m k_B T)^{3/2}} \end{aligned} \quad (28)$$

There's nothing special about the k th particle, and exactly the same expression would have been obtained for any other particle (but with a different subscript on the momentum variable), so we may as well remove the subscript k , and just use the symbol \mathbf{p} , which will now refer to the momentum of *any* particle. In other words, the momentum distribution (i.e., probability to observe p) for any particle is

$$p(\mathbf{p}) = \frac{e^{-\beta \mathbf{p}^2 / 2m}}{(2\pi m k_B T)^{3/2}} \quad (29)$$

Of course, what we're really interested in is the probability of some particle having a *speed* v (because the direction of travel is not so important), which is defined as $v = m^{-1} \sqrt{p_x^2 + p_y^2 + p_z^2}$. We can easily derive the distribution of v from Eq. (29) using the delta function (which selects those values of the magnitude of \mathbf{p} that have the value v):

$$p(v) = \frac{1}{(2\pi mk_B T)^{3/2}} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z e^{-\beta(p_x^2 + p_y^2 + p_z^2)/2m} \delta(v - m^{-1} \sqrt{p_x^2 + p_y^2 + p_z^2}) \quad (30)$$

We can now use the spherical coordinate transformation of Eq. (13), with $N=1$, to convert Eq. (30) to

$$p(v) = \frac{1}{(2\pi mk_B T)^{3/2}} \int_0^{\infty} dp p^2 \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta e^{-\beta p^2/2m} \delta(v - m^{-1} p)$$

which after carrying out the trivial angular integrals and then the integral over p (using the change of variable $p = mv$) leads to

$$p(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} \quad (31)$$

This is the Maxwell-Boltzmann speed distribution, and it has exactly the structure of the curves seen in the experimental graph above.